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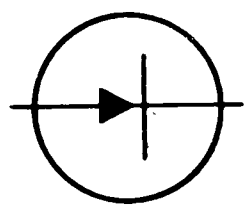

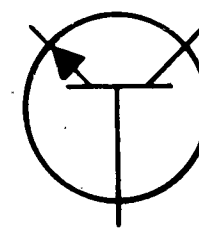

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1306 Farr Drive

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Interim Technical Documentary
Progress Report No. 5

GALLIUM ARSENIDE DENDRITE SINGLE CRYSTAL PROGRAM

Contract No. AF 33 (657)-8162

Period Covered
25 February to 24 May 1963

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ABSTRACT

During the past quarter, greater effort has been placed on the preparation of gallium arsenide web dendrites. The top contact grids on the solar cells have been refined.

All three furnaces were in operation during this report period. An examination of the results used indicated that some changes in furnace design were necessary. The effect of the changes which were made have been evaluated.

Some improvement has been obtained in the character of the dendrites pulled.

I. INTRODUCTION

Several GaAs dendrites, 2 to 8 inches long, were pulled to learn more about the effect of thermal geometry, supercooling, pull rate, and stoichiometry on dendrite and sheet growth. As a result of these experiments and the previous experience with the growth of multi-dendrite sheet, extensive modifications in the pulling furnaces have been made and are currently being evaluated. Experiments during the past quarter have confirmed that the side-arm As control scheme has eliminated stoichiometry problems in the 14" furnaces.

II. DENDRITE PREPARATION

A. Experimental Problems and Progress

1. Growth of Dendritic Material

Much material of a nature similar to that previously obtained has been pulled during this report period. This material has been examined for twin structure and gallium inclusions. The twin structures had both odd and even numbers of twins and, in general, it can be said that the material pulled showed a configuration similar to the seed used. In the material pulled after side-arm control zones were used on all furnaces, the presence of gallium inclusions vanished when the control temperature was maintained at or above the value necessary to give stoichiometric melts.

Some runs yielded material of greater length and more apparent perfection than seen before. Figures 1 and 2 show the two faces of a portion of a dendrite which was pulled at a rate 5"/min from a primitive growth onto an untwinned GaAs seed. It can be seen from the photographs of this dendrite that, while the two surfaces (Fig. 1 Ga; Fig. 2 As) show fine structure differences, the greater differences previously seen are not apparent. This dendrite has been carefully examined for twin structure and shows three sets of closely spaces twin paris. This material has been, in part, reserved as seed material and a measurement of doping level and mobility has been made. The mobility is 3000 cm^2/volt-sec, the impurity level is 5.7×10^{16} per cc. and the resistivity is 0.037Ω-cm.

Figure 3 shows the arsenic face and Figure 4 the gallium face of a three-inch dendrite pulled at a pull rate of 5" to 6" per minute. This dendrite shows some wing growth quite similar to that seen on some of the dendrites of

silicon pulled early in the work with silicon and indicate that more rapid pull speed would be advantageous. The wing growth on this dendrite and many similar ones led to the decision to modify the pulling mechanisms of the furnace so the pull speed could be increased.

Figure 5 shows a dendrite pulled at an increased pull speed of the order of 10" per minute and this shows none of the wing growth seen in the dendrite pictured in Figures 3 and 4. In Figure 5 the left hand picture is the arsenic face, and the right hand picture the gallium face and the normal wide and narrow structure on the respective faces can be seen.

In each of the pulls pictured, the materials represent the full pull length at the time of pulling due to the length of seed. Since this was the case it was decided to make the changes in the furnaces necessary to give greater pull length.

As was discussed in the previous report period, multi-dendrite web structures were obtained using seeds with narrow twin spacings. In the case of the other materials pulled (germanium, silicon and indium antimonide), the use of a narrow twin spacing prevents multi-dendrite web from forming. The cause of this growth phenomenon in gallium arsenide remains unexplained. Changes have been made in the system to try to grow dendrites under more controlled conditions since it is felt that better control of growth conditions for dendrites would yield a condition conducive to better web growth.

2. Modification and Operation of Pulling Furnaces

7" Exploratory Furnace

The above designation is no longer descriptive of this furnace since major changes have been made during this report period. The major

changes in furnace design involved conversion to a side-arm arsenic control zone, change in the pull length available and change in the tube and crucible assembly dimensions. The details and the results of these changes will be taken up in order.

(a) In the previous periods some very preliminary results were reported in connection with stirring experiments which were carried out. The purpose of the stirring was to give a more homogeneous melt with a shorter induction period before pulling could be started. A more detailed discussion of the results of this work is given in a later portion of this report. The effect of stirring the melt proved to be less important in homogenizing the melt than changing the position of the arsenic control zone. With the zone located below the crucible assembly and the control temperature based on loss of heat by radiation rather than heating, the control temperature reading was very questionable and the diffusion of the arsenic gas past the closely fitting crucible-shield assembly very slow. The poor relationship between the actual control temperature and the temperature read gave poor stoichiometry control and prevented reasonable estimation of the pressure of arsenic in the system. The slow diffusion of arsenic gas past the crucible-shield assembly caused the time for attainment of stoichiometry to be very long. A side-arm placed above the crucible assembly (as shown diagramatically in Fig. 3, Progress Report No. 4) was not affected by radiation from the hot crucible and the temperature was more easily controlled at the desired value. The value of the control temperature read at the thermocouple showed a much closer ($\pm$ 2°C) correspondence with the actual temperature of the arsenic in the control zone. Using the side-arm control zone, the results

indicate that stoichiometry is reached and maintained in the system within 1/2 hr. after all the heaters reached equilibrium, as opposed to the several hours necessary using the earlier system. Another advantage is that the set temperature to reproduce the condition of stoichiometry remained constant and was independent of the amount of arsenic present; this previously had not been the case.

(b) The pull length of this furnace has now been increased to afford the opportunity of pulling longer dendrites and webs. In several of the past pulls prior to and during this report period, material has been obtained using the full potential length of the furnace. In view of this fact, it was decided to provide the means of continuing the pulls over longer times and lengths to provide more material and to enable the pulling conditions to equilibrate more. The system has been installed and checked out mechanically.

(c) In attempting to make an adjustment in the temperature profile, changes have been made in crucible covers and rings above the crucible. There has been, in each change, some merit and improvement in pulling conditions, but the optimum situation has not been arrived. Since the second furnace (previously designated as the 14" furnace) had identical dimensional configuration with this furnace, it was decided that more fruitful results might be obtained by adjusting the temperature profile with a different approach in this furnace while continuing the previous work in the second furnace. The decision having been made to make a big change and follow a new approach, a crucible of larger cross-section and the larger tube necessary to use it has been installed. The determining factor on the size and configuration of the new crucible was that a system basically identical to that used in producing

silicon web would be a starting point since the effect of changes in such an apparatus are well known in work with silicon. The new system has been set up and is ready to be checked out.

(d) An attempt was made to use a specially designed slotted graphite shield on top of the crucible in place of the quartz ring and its associated graphite ring. This system did not heat sufficiently to prevent clouding of the tube and we have gone back to the previously used system.

(e) A quartz enclosed tantalum cover is being used in place of the graphite cover previously used. This tantalum cover has been used in several runs, but its effect has not been fully evaluated due to other factors having had more effect on the runs. Qualitatively, it seems to work at least as well as the graphite cover.

(f) The pulling mechanism has been changed to give increased pull rates since some of the growth patterns observed indicated that a faster pull speed would be advantageous.

Fourteen-inch Furnace

As noted in the last quarterly report, problems have been encountered due to a poor temperature gradient in the melt, with the surface being too cold. Many adjustments were made in the RF coil location, cover configuration and location, and in the location and thickness of the graphite ring being used to heat the furnace tube above the crucible to prevent clouding of the sight hole. Improvement of the thermal conditions was obtained.

Most of the pulls made in this furnace during the period were for the purpose of yielding seeds of different configuration since good seeds

represent a necessary element to pulling continuous dendritic material and web.

Since this furnace was the first furnace utilizing the side-arm control zone for arsenic, a large number of samples of dendritic material were evaluated in terms of gallium or arsenic inclusions. When the temperatue of the arsenic control zone is maintained at a prescribed minimum level or above (discussion of arsenic pressure in equilibrium with gallium arsenide in later portion), no gallium inclusions have been detected in dendrites. The dendritic materials were potted and lapped and polished and examined microscopically for gallium or other inclusions. The polished samples were also stained and the twin structures determined.

In no cases, even with arsenic pressure well above that required for a stoichiometric melt, were inclusions of arsenic found. It is likely that the extremely high vapor pressures of solid or liquid arsenic at the melt temperature would prevent any build up of arsenic concentration in front of the growing interface. Since the likelihood of build up of arsenic concentration is low, an inclusion of arsenic in the growing crystal is unlikely.

Twenty-four Inch Furnace

During the quarter, a variety of dendritic material has been grown in the 24-inch furnace. Seeding continuous growth to a dendritic seed has been difficult, so that most of the material produced has been primitive growth. In one run eight inches of dendritic material was grown with apparent ease. Unfortunately, the material which was grown had only two twin planes, not three twin structure which is desired.

Thermometry for the control of the melt temperature has been one of the major technical problems with the 24-inch furnace during the past quarter. The furnace was initially designed to use a Pt/Pt-10% Rh thermocouple to sense the crucible temperature. The choice of the thermocouple rather than a radiation sensing device was made on the basis that the thermocouple output is inherently more stable on both a long-term and short-term basis; and furthermore, provides a better indication of the absolute temperature and of temperature increments. The thermocouple is, however, subject to attack by the arsenic atmosphere of the furnace, and was therefore protected by a fused quartz tube. Several slight modifications were made to the original design before arsenic contamination ceased to be a problem.

While awaiting appropriate design changes, the furnace was temporarily converted to use a radiation sensing element. As expected, the output of the sensor varied greatly from run to run and also drifted badly during a given run. In some cases the apparent melting point drifted as much as 50°C in the course of several hours. This is to be contrasted with a day-to-day stability of several degrees which was obtained with the Pt-Pt-10% Rh couple.

The material which has been grown to date in the twenty-four inch furnace has always shown gallium inclusions. A careful measurement of the arsenic control zone temperature profile indicated that the arsenic temperature should be very close to the indicated control temperature. During operation, the arsenic was usually maintained slightly above the temperature required for a stoichiometric melt. Under these circumstances, it is rather difficult to understand why the resulting crystals should display an excess of gallium.

Two tentative explanations are proposed, and both have to do with the fact that arsenic is lost from the furnace through the seals. The first possibility is simply that the system runs out of arsenic. The samples that are usually examined are those that are grown near the end of an operating day. By this time the furnace has been in operation for six hours or so, and the possibility exists that the arsenic reservoir is depleted. Direct observation of the reservoir indicates that some arsenic is usually left at the end of a run; however, the quantity is much less than the initial amount. Also, since the thermocouple plug must be removed from the reservoir, there is no assurance that the arsenic observed was actually in the reservoir during operation and has not merely condensed during the short interval between the removal of the plug and observation.

A second possibility for an anomalously low arsenic pressure is related to the kinetics of evaporation from solid arsenic. If arsenic is lost from the system at a sufficiently rapid rate, then evaporation from the arsenic reservoir may be too slow to maintain equilibrium pressure. Evidence for such a possibility is given by Brewster and Kane[1] in reporting the results of Knudsen cell experiments. They found that with an aperature to surface ration near unity, the apparent vapor pressure of arsenic was over two orders of magnitude lower than the equilibrium pressure; even with ratio of 10^{-3} they found a one order of magnitude difference.

Lowering the arsenic loss rate would eliminate both of the above effects. Unfortunately, the installation of tighter fitting pistons has not materially reduced the loss, nor has the use of higher argon pressure. Merely increasing the size of the arsenic charge should help matters if insufficient arsenic is the problem. Some slight improvement was noted when a 50 gram charge was used; however, the results are not conclusive.

3. Seeds and Seed Holders

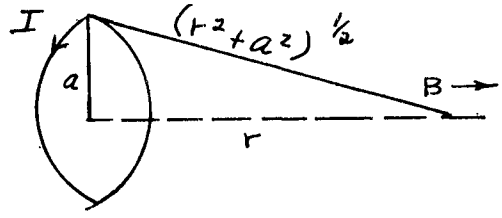
The seeds previously used have been welded to the end of a 1/16" x 1/16" x 2" bar of gallium arsenide. This has been done for several reasons; one being that the seeds were too short to be held in the chuck being used, a second being that the use of the long gallium arsenide rod kept the chuck which was made of lavite (a natural ceramic) from coming too close to the melt and possibly contaminating it. A new type of chuck and less brittle dendrite (due to elimination of gallium inclusions) has allowed the use of dendrites as seeds.

Use of this new chuck potentially introduces the possibility of melt contamination, but this is not considered a critical factor at this time. The fact that the new chuck permits the utilization of much smaller seeds and eliminates a tedious and, at times, difficult welding operation makes its use highly desirable.

4. Melt Stirring

In the stirring experiments carried out during the past two report periods, 60 cycle A.C. current was used. The use of 60-cycle current removed the problem of assembling special 400-cycle or 1000-cycle equipment. The torque, however, exerted on the liquid by an A. C. field is proportional to the frequency; low frequency giving less stirring, and since the space available around the furnace was also limited, economic use of this space was absolutely necessary to obtain stirring. Calculations were, therefore, carried out to determine the most suitable type of coil winding. These calculations are as follows:

For a magnetic field on the axis of a circular loop in vacuum (approximately correct for air), the field B is given by:



$$B = \frac{I}{10} \int_0^{2\pi} \frac{a \, d\phi}{(a^2 + r^2)} \cdot \frac{a}{(a^2 + r^2)^{1/2}}$$

$$B = \frac{2\pi I a^2}{10 (a^2 + r^2)^{3/2}}$$

If current is not a limiting factor, a figure of merit from this equation is $a^2/(a^2 + r^2)^{3/2}$. It is possible now, using this factor, to construct a curve showing the relative importance of any turn in a coil; thus a coil can be wound with the most efficient geometry. If the power to the coils is also limited, then for any voltage the length of the coil determines the current in the coil which in turn affects the torque produced. Thus, for a limited transformer output the permissible length of winding can readily be calculated, and a second geometric construction can be made which shows the relative importance of any turn in a coil of limited conductor length. Both of these types of curves are shown in Figure 6, the solid curves give the relative importance of a turn where conductor length is not restricted and the broken curves give the same for a coil of restricted length. The shaded rectangle shows the position of the windings in the coil used for stirring the gallium arsenide melt. This coil is the most efficient coil which could be built in the volume of space and the restricted length of conductor available. Good stirring of the melt was achieved.

As mentioned in an earlier portion of this report, the change in the position of the arsenic control zone had a great effect on the length of time necessary for melt homogenization. The stirring did not seem to change this time appreciably and the space required by and the localized cooling effect of the coils made the overall effect of questionable value. Stirring coils have thus been eliminated from the designs currently in use. The technique can be incorporated on later, more permanent furnace designs if it appears profitable.

B. Some Comments on Arsenic Pressure Control

In all the furnaces the melt composition is controlled by adjusting the temperature of an arsenic reservoir. This dew-point method of control requires a knowledge of both the equilibrium dissociation pressure of GaAs and of the vapor pressure of arsenic as a function of temperature. The vapor pressure of arsenic as cited in most references, e.g. Kelley[2] derives mainly from the work of four investigators.[3-6] As a result, there is reasonable agreement in the literature for this parameter. The equilibrium dissociation pressure of GaAs has also been studied; however, there is some disagreement as to the value at the melting temperature of the stoichiometric material. As an example, the reference most often cited is Van den Boomgaard and Schol[7] who give a melting temperature of 1237 $\pm$ 3°C and a dissociation pressure at that temperature of 685 Torr. The work of Richman, however, gives a dissociation pressure of at least 740 Torr, although the melting temperature of 1238° is in good agreement with the other work.

This discrepancy appears to be the result of the experimental techniques used for the measurement and the interpretation of the data. The

data of Van den Boomgaard and Schol were based on observations which were primarily dew-point observations. The data of Richman, on the other hand, were direct-pressure measurements by a quartz Bourdon gauge. When the data of Boomgaard and Schol is examined, it is found that they not only quote arsenic pressure values, but also give the arsenic reservoir temperatures. An examination reveals that the pressure values quoted are not in agreement with the arsenic pressure data mentioned above.

A plot of the Boomgaard and Schol arsenic temperature and melt composition data, Figure 7, reveals that an arsenic reservoir temperature of 608°C is in equilibrium with stoichiometric GaAs. This temperature corresponds to a pressure of about 730 Torr according to the data of Kelley. Thus, there would appear to be no actual disagreement with the results of the two references.

III. SOLAR CELL PREPARATION

The width of the top contact grid strips on the solar cells have been reduced to .005"; new masks were made for this purpose. The masks and GaAs wafers were allowed to rest in a V-block which was heated to about 200°C during the silver evaporation step in the bell jar. It was found that cell series resistances were already too low to be further reduced by solder coating the grid lines and bottom contacts.

IV. RESULTS AND CONCLUSIONS

The three furnaces were operated during this period and some material pulled. On the basis of the characteristics of the material and the

way the furnaces acted during the pull, changes have been made and tested. Some improvement has been noted in the ease of pulling and in the character of the material.

A technique for applying thin contacting strips to the surfaces of GaAs solar cells has been developed.

V. PROGRAM FOR FUTURE WORK

When the evaluation of the effects of the furnace changes have been completed, further attempts will be made to pull gallium arsenide webbed dendrites. Any additional changes necessary to improve the material will be made.

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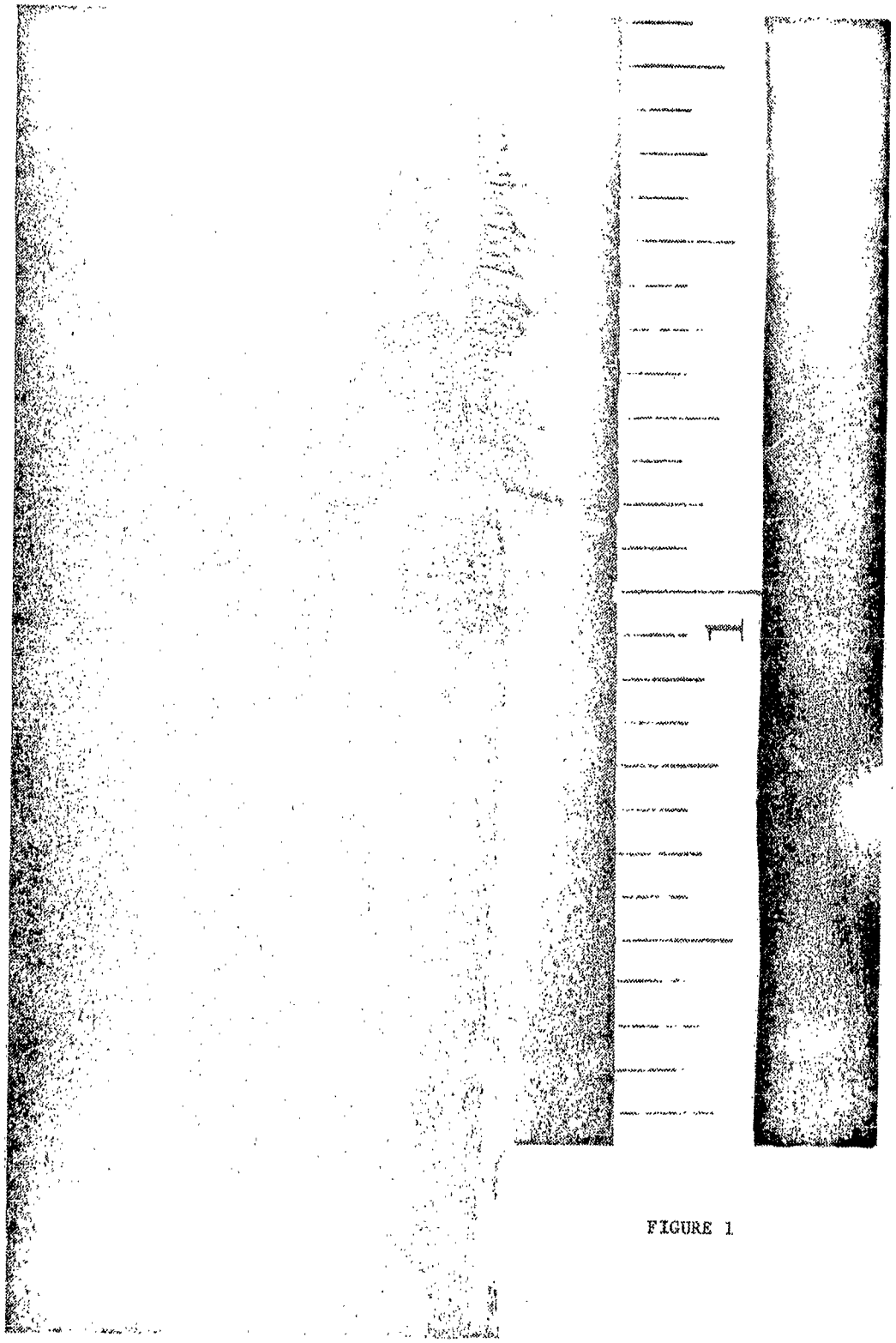
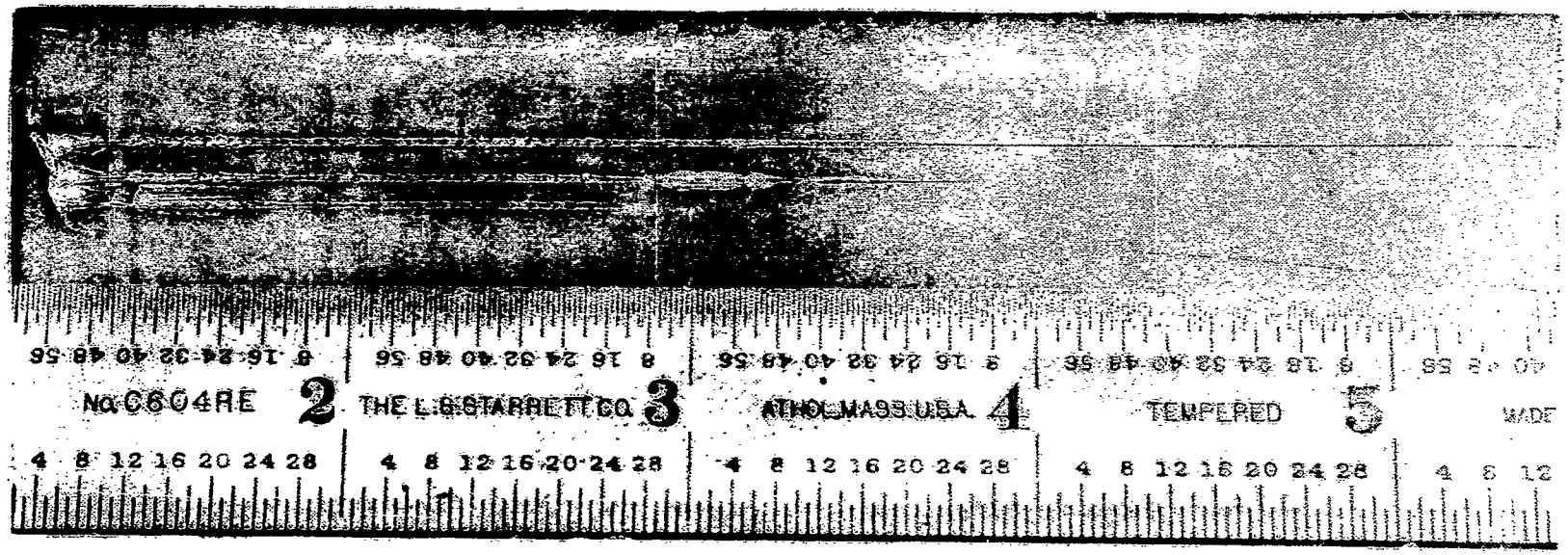


FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4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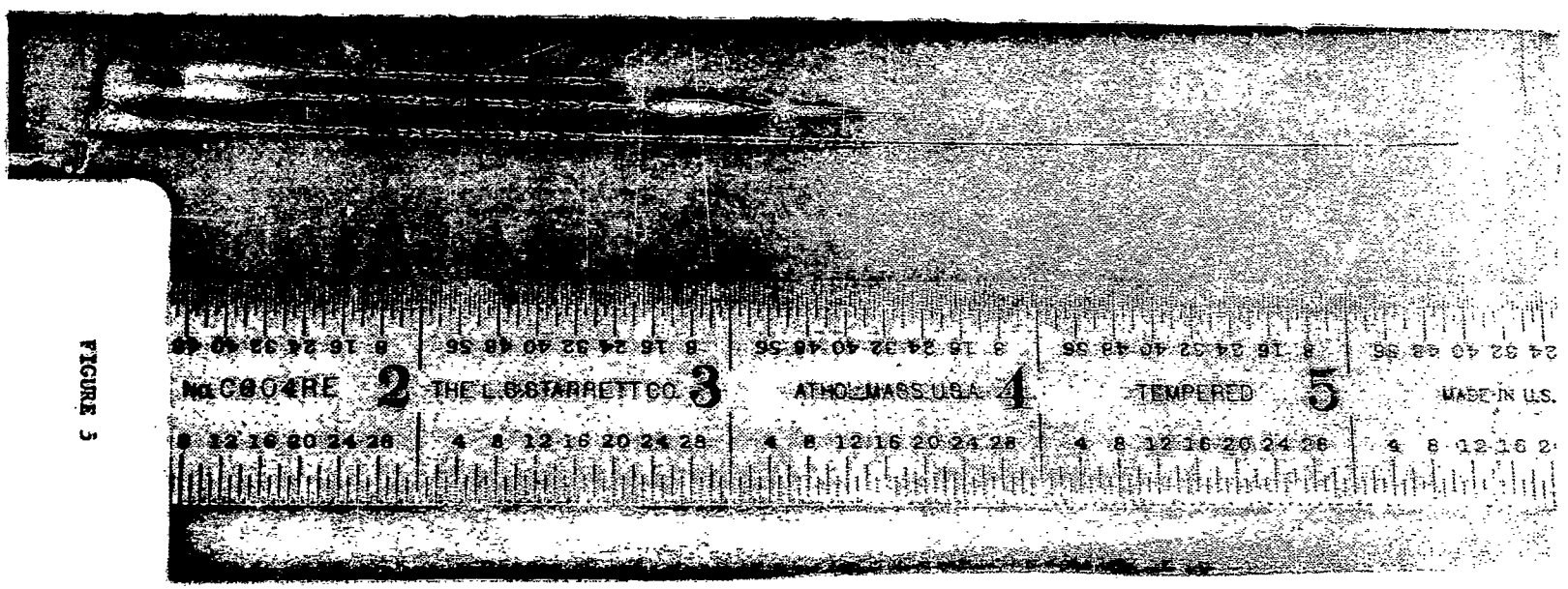
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FIGURE 5

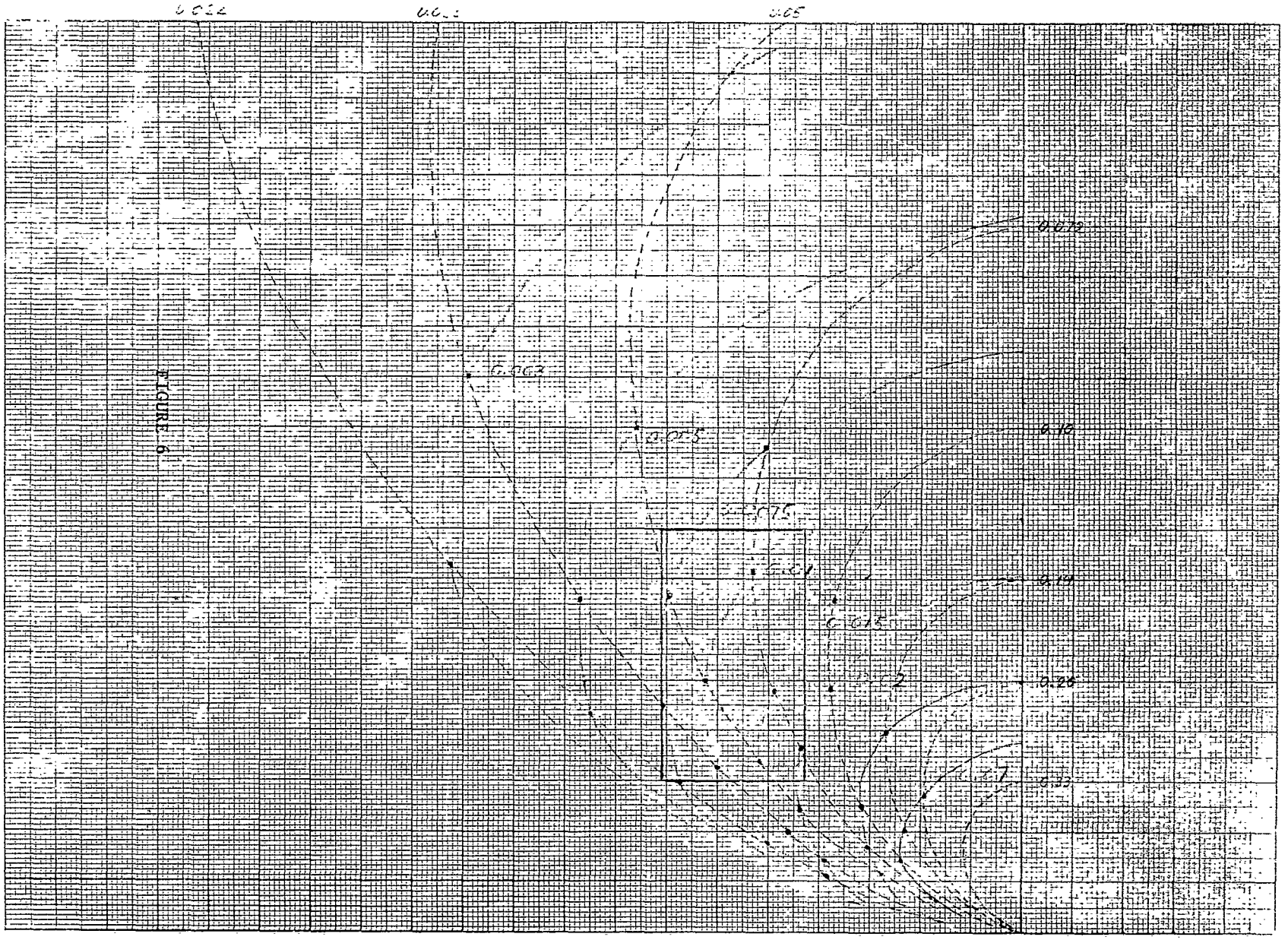

FIGURE 9

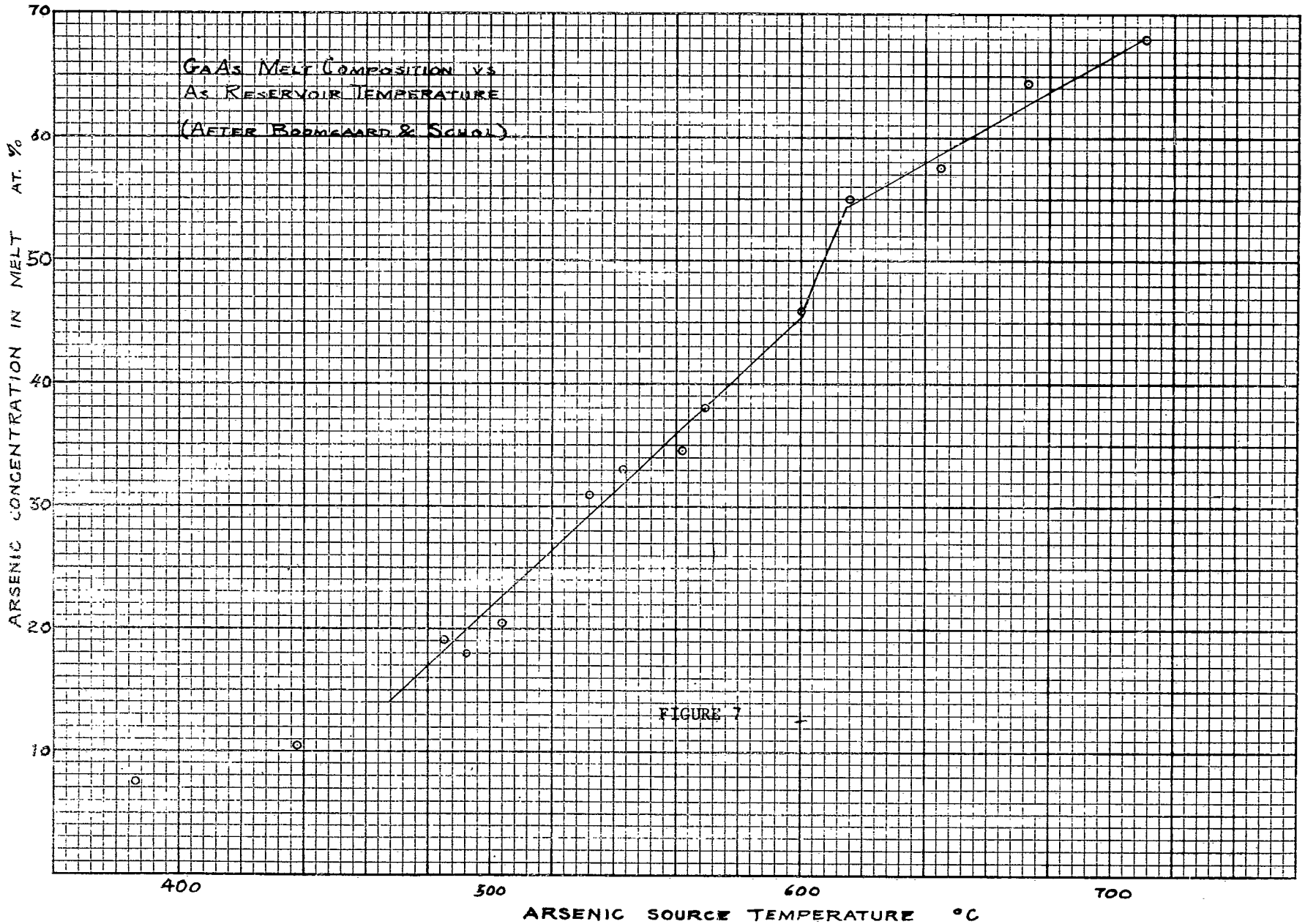
GaAs Melt Composition vs
As Reservoir Temperature
(After Boomgaard & Schol)
ARSENIC CONCENTRATION IN MELT AT. %
70
60
50
40
30
20
10
400
500
600
700
ARSENIC SOURCE TEMPERATURE °C

FIGURE 7

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